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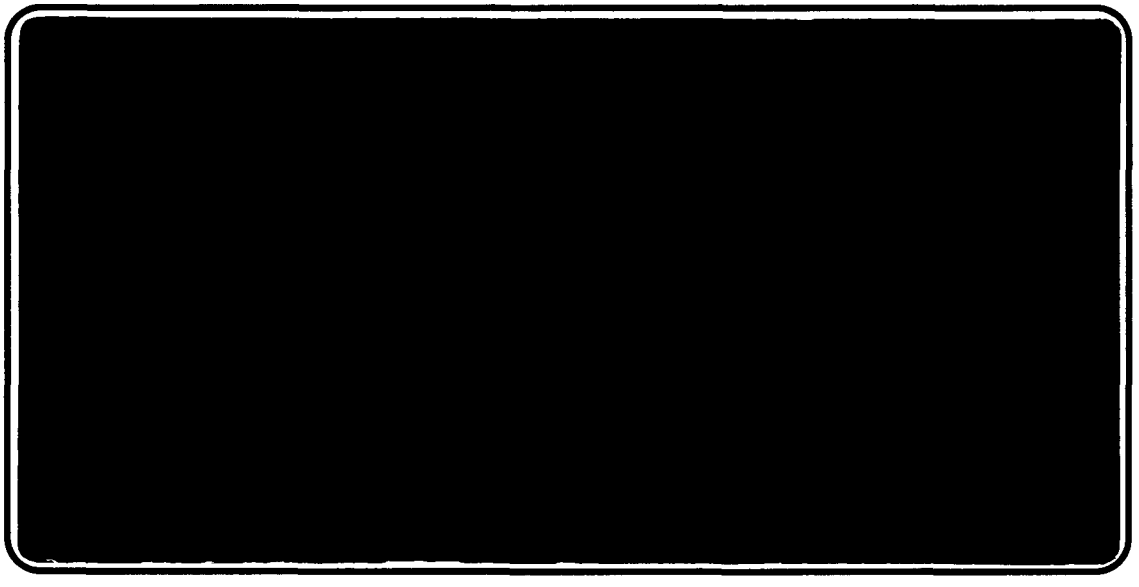

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FORMATION OF CHLORINATED DIOXINS AND FURANS IN KRAFT PULP BLEACHING

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INTRODUCTION

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) and The Institute of Paper Science and Technology (IPST) have jointly undertaken laboratory bleaching studies to achieve an improved understanding of the factors affecting the formation of polychlorinated dibenzodioxins and dibenzofurans (collectively, "dioxins"). These studies deal with the source and fate of dioxins, the effect of chlorine dioxide on dioxin precursors, effects of chlorination stage conditions, and mixing effects.

SOURCE AND FATE

Our early studies were aimed at identifying the points in the bleaching sequence at which dioxins were formed, determining the extent to which they originated from the corresponding unchlorinated precursors, and learning whether they were either formed or destroyed in the caustic extraction stage of the bleaching sequence.

Unbleached (kappa no. 32) softwood kraft pulp was provided by a north-central mill. Duplicate samples of the pulp were chlorinated in a Quantum Technologies laboratory mixer and subsequently caustic-extracted in a stainless steel reactor equipped with a horizontal shaft pin mixer. No chlorine dioxide was used in the chlorination stage and no oxidants were added to the extraction stage; otherwise, typical mill conditions were used. Bleaching was carried out in an enclosed area with a controlled air supply, and all equipment that contacted either the pulp or the effluent was rinsed with toluene and either methanol or ethanol before and after contact. The after-contact rinsates were combined and reserved for analysis.

Effluents were collected from each stage by dilution and thickening. Thickening was accomplished by filtration through a stainless steel wire mesh on a Buchner funnel, the filtrate being passed twice through the pad to minimize the amount of fiber and fines in the filtrate. Samples of the effluents, pulps and rinsates were transferred to ultraclean glass containers and shipped to NCASI's organic analytical facility in Corvallis, Oregon, for determinations of polychlorinated (tetra- through octa-) dibenzodioxins and dibenzofurans.

To assess the importance of dibenzodioxin (DBD) and dibenzofuran (DBF) as precursors for the corresponding chlorinated compounds, another sample of the same unbleached pulp was diluted with water which had been spiked with a methanol solution of DBD and DBF. After filtration, the resulting pulp was bleached exactly as described above for the control sample.

A third sample of pulp was treated to reduce its DBD and DBF contents to the lowest levels possible. It was extracted overnight (approximately 50 cycles) with high purity methanol in a soxhlet extractor. The extracted pulp was then diluted with reagent grade water and the liquid phase was partially distilled. More water was added and distilled, and the cycles of water addition and distillation were repeated until all methanol had been removed from the pulp, as indicated by the boiling point. The resulting extracted and steam-distilled pulp sample was then bleached, using the same conditions as for the control.

The experimental program described above was repeated in its entirety, to provide an independent replicate of all results. This allowed confirmation of the results of the first replicate, and put the conclusions on a firm basis.

Partial results of the control bleaches are shown in Figure 1. The chlorinated pulps contained an average of 37 micrograms 2,3,7,8-tetrachlorodibenzodioxin (2378-TCDD) per metric ton (parts per trillion) of pulp while the amount in the chlorination stage effluent was barely detectable, at 0.9 ppt. The duplicate bleaches agreed reasonably well, leading to the conclusion that virtually all of the 2378-TCDD

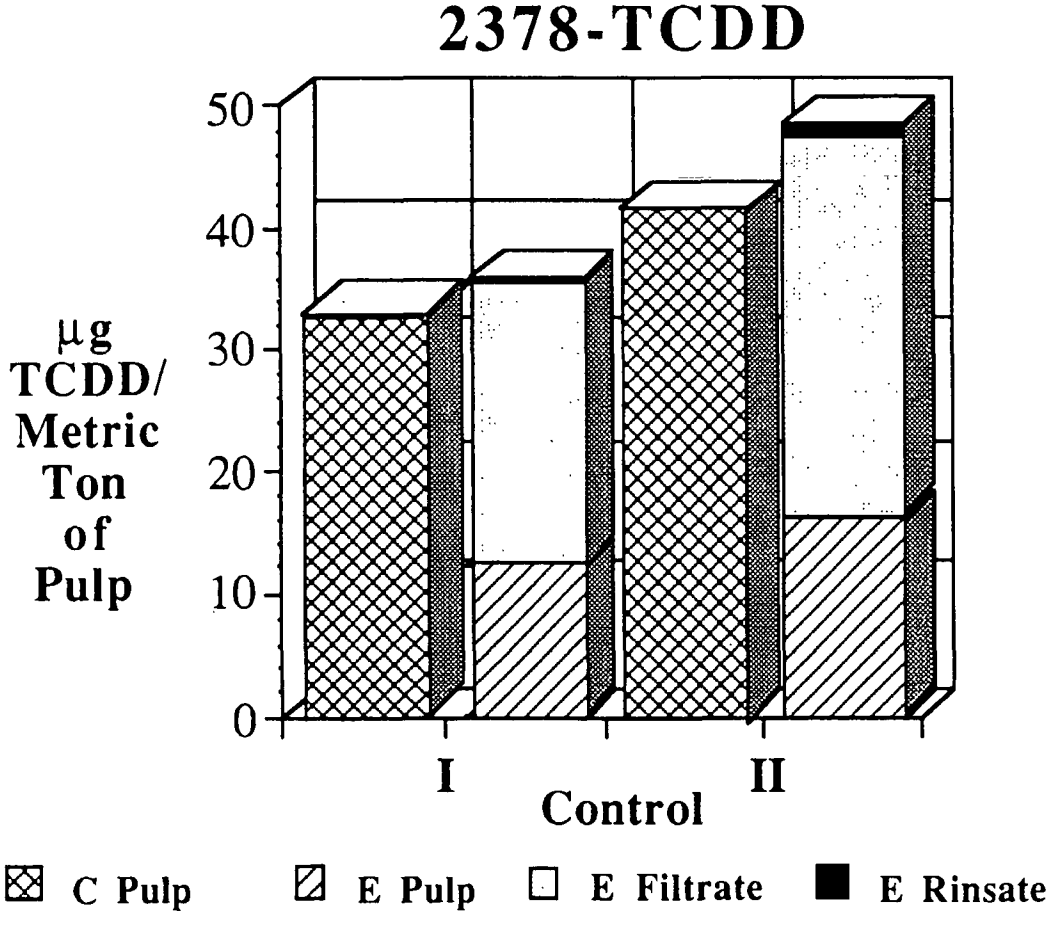

Figure 1. 2378-TCDD emerging from chlorination (C) and caustic extraction (E) stages in laboratory bleaches of a mill-produced softwood kraft pulp. Data for two independent replicate experiments (I and II) are shown. 2378-TCDD was virtually absent from the C filtrate.

leaving a chlorination stage is likely to be found in the pulp. The situation downstream of the extraction stage is quite different, however. There, the amount of TCDD in the effluent is greater than that found in the pulp. The total amount of 2378-TCDD emerging from the E-stage averaged 42 ppt, providing little evidence for either formation or destruction of this compound during caustic extraction. Very little was found in the solvent rinsates, indicating that adsorption on equipment surfaces was not as great a problem as we had feared.

Figure 2 compares these same data with the results of the bleaches of the spiked pulp. Bleaching of this pulp, which had a DBD content 50 times higher than that of the control, gave pulp, effluent and rinsate 2378-TCDD levels approximately 30 times higher than in the control, confirming earlier reports from other laboratories of the importance of DBD as a dioxin precursor. We observed a similar enhancement of 2378-TCDF formation as a result of the DBF spike. Also confirmed by the results of these experiments were the above conclusions regarding partitioning of dioxin between pulp, filtrate and rinsate, and lack of formation or destruction of dioxin in the E-stage.

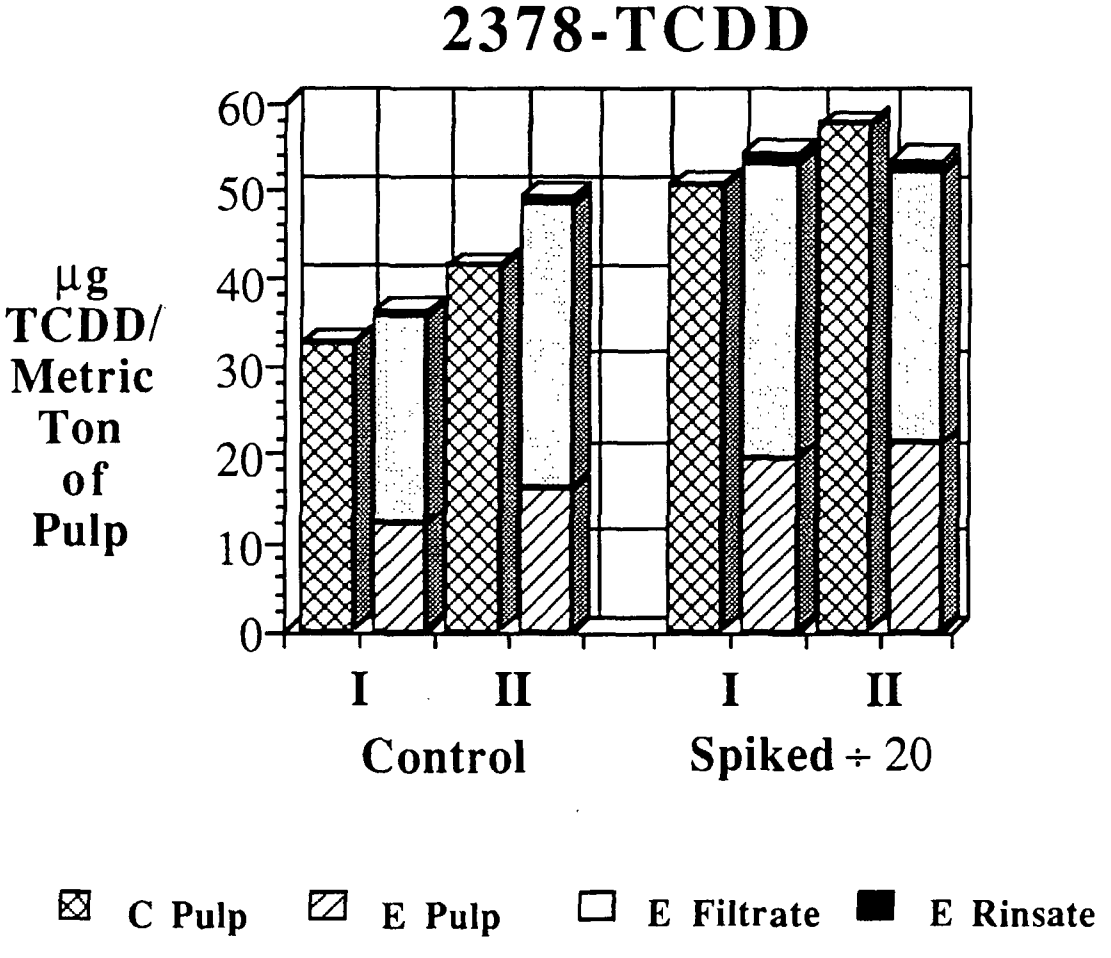

Figure 2. Comparison of 2378-TCDD levels in the control experiments (4 leftmost columns, from Figure 1) with the corresponding data from experiments in which the pulp was spiked with DBD before bleaching.

Bleaching of the exhaustively extracted and steam distilled pulp samples gave the results shown in Figure 3. Careful analysis of the unbleached pulp showed that DBD was not detectable at a detection limit of 0.6 ppt. Nevertheless, as shown in the figure, it generated 20 ppt of 2378-TCDD when it was chlorinated. The most straightforward interpretation of this result is that 2378-TCDD was formed from some precursor other than DBD. Another possibility is that DBD is formed during the chlorination stage, while a third is that the extracted pulp still contained DBD that could not be detected by the analysis. In any case, the dioxin formed in these experiments had a nonextractable precursor.

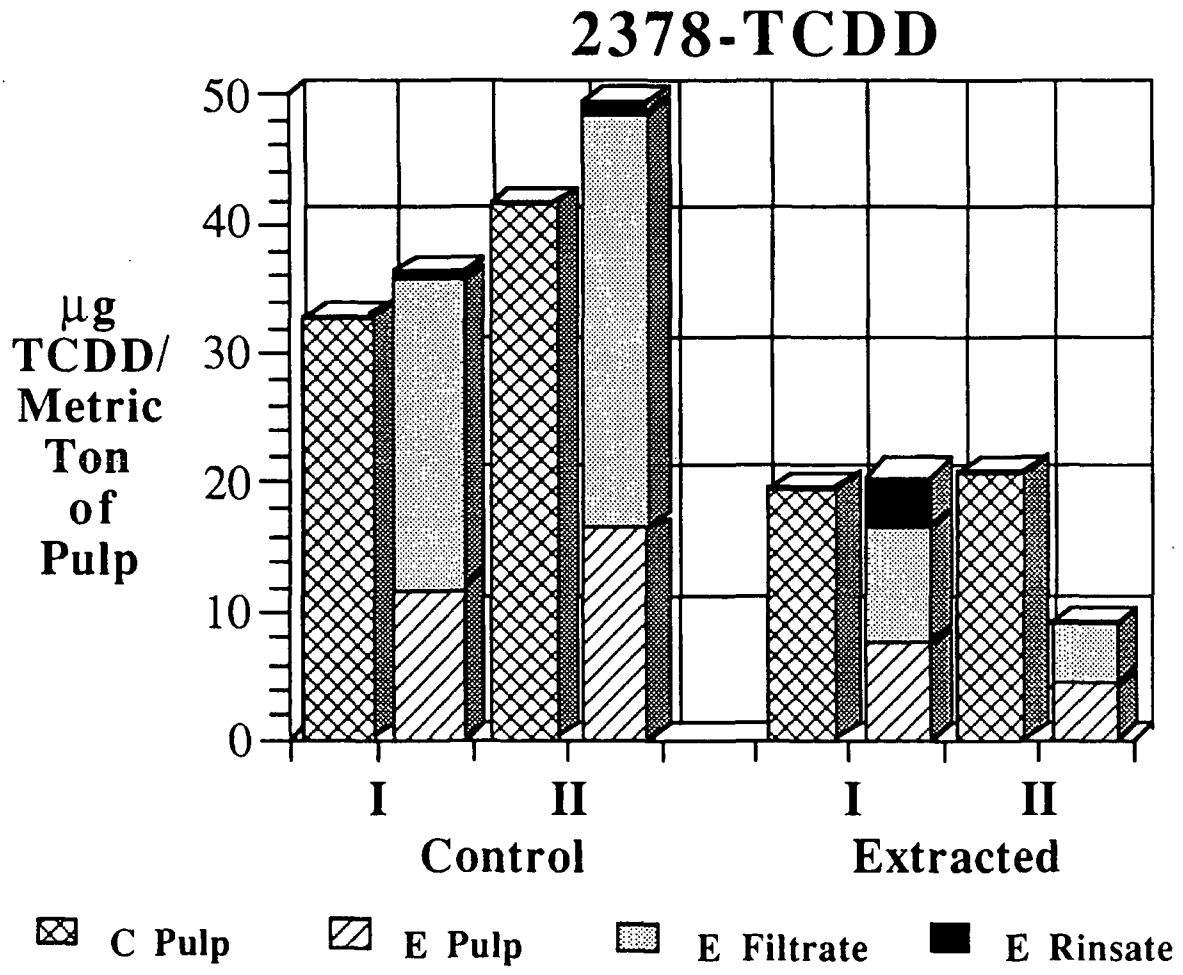

Figure 3. Comparison of 2378-TCDD levels in the control experiments (4 leftmost columns, from Figure 1) with the corresponding data from experiments in which the pulp was exhaustively solvent-extracted and steam distilled.

Another indication of the existence of non-DBD precursors may be found by comparing DBD and TCDD levels. Table 1 contains a summary of the results of DBD and 2378-TCDD determinations on the unbleached and bleached pulps, respectively. The results for the spiked pulp correspond to a 35% molar yield (62% weight yield) of 2378-TCDD from DBD. On this basis, the 34 ppt of DBD should have given rise to 21 ppt of 2378-TCDD, not the average of 37 ppt actually observed. The difference of 16 ppt, which may have arisen from other precursors, agrees with the 20 ppt

observed upon chlorination of the apparently DBD-free pulp. On the other hand, the "fingerprint" or distribution of the various dioxin and furan isomers was similar for all pulps bleached, lending weight to the argument that DBD and DBF were the precursors in all cases. Further research is needed to distinguish between the three precursor hypotheses.

TABLE 1. DBD in Brownstock and 2378-TCDD Formed.

	DBD in Brownstock µg/Tonne	2378-TCDD Formed µg/Tonne
Extracted	ND (0.6)	19.7
	ND (0.6)	20.8
Control	34	32.8
		41.5
Spiked	1740	1011
	1750	1150

EFFECT OF ClO_2 ON PRECURSORS

It has been shown elsewhere that substitution of chlorine dioxide for part of the chlorine in the chlorination stage leads to decreased formation of dioxins. If the mechanism of this effect were known, it may point the way to other dioxin control methods. One possibility, destruction of precursors by chlorine dioxide, was the subject of our experiments in this area.

To determine whether chlorine dioxide destroys precursors, we designed an experiment involving 2 series of 3-stage chlorinations. The trials within a given series differed from one another only with respect to the total amount of molecular chlorine (Cl_2). Each trial consisted of an initial chlorination, the same for all trials, in which the amount of chlorine applied to the pulp was equal to 0.12 times the kappa number of the unbleached pulp or, in other words, the kappa factor was 0.12.

In one series, this was followed by a second stage, initiated by injecting chlorine dioxide solution 30 minutes after injection of the initial chlorine charge. The amount of chlorine dioxide injected was constant and equivalent to a kappa factor of 0.08. Thirty minutes later, the third stage was initiated by injecting a solution of molecular chlorine. The kappa factor in the third stage was varied from 0 to 0.16. Table 2 summarizes this series.

TABLE 2. Three-Stage Chlorination Experiments.
Active Chlorine/Kappa No.
Stage 1: Cl_2/Kappa No.=0.12

Stage 2, ClO_2	Stage 3, Cl_2	Active Cl Kappa	Cl_2 Kappa
0.08	0.00	0.20	0.12
0.08	0.06	0.26	0.18
0.08	0.08	0.28	0.20
0.08	0.12	0.32	0.24
0.08	0.16	0.36	0.28

The rationale underlying this scheme was that the initial chlorine charge would satisfy most of the oxidant demand of the lignin in the pulp, while being low enough not to generate any TCDD or TCDF; work in other laboratories has shown that dioxins are formed only if the kappa factor is greater than about 0.15. This was necessary to prevent the subsequent charge of chlorine dioxide from being rapidly consumed by lignin before it had an opportunity to react with dioxin precursors (assuming it had the power to do so). The final stage of chlorination was designed to serve as an indicator of the presence of precursors; if still present, they would result in TCDD and TCDF being found in the chlorinated pulp.

To provide a basis for comparison, a second series of 3-stage chlorinations was done. This series was identical to the first, except that pure water was injected for the second stage, instead of chlorine dioxide solution. These trials are summarized in Table 3.

TABLE 3. Three-Stage Chlorination Experiments.
Active Chlorine/Kappa Number
Stage 1: Cl_2/Kappa No.=0.12

Stage 2, ClO_2	Stage 3, Cl_2	Active Cl Kappa	Cl_2 Kappa
0.00	0.00	0.12	0.12
0.00	0.06	0.18	0.18
0.00	0.08	0.20	0.20
0.00	0.12	0.24	0.24
0.00	0.16	0.28	0.28

The results of 2378-TCDD analyses on the chlorinated pulps are presented in Figure 4. Note that the TCDD levels are plotted against the *molecular* chlorine (Cl_2) charge divided by the unbleached kappa number, a ratio which is referred to as chlorine factor. It is apparent from the figure that chlorine dioxide pretreatment *increases* the amount of TCDD formed from a given amount of molecular chlorine. Although not included here the corresponding graphs for 2378-TCDF and 1278-TCDD were very similar in appearance to Figure 4. Collectively, they show that chlorine dioxide fails to destroy dioxin precursors.

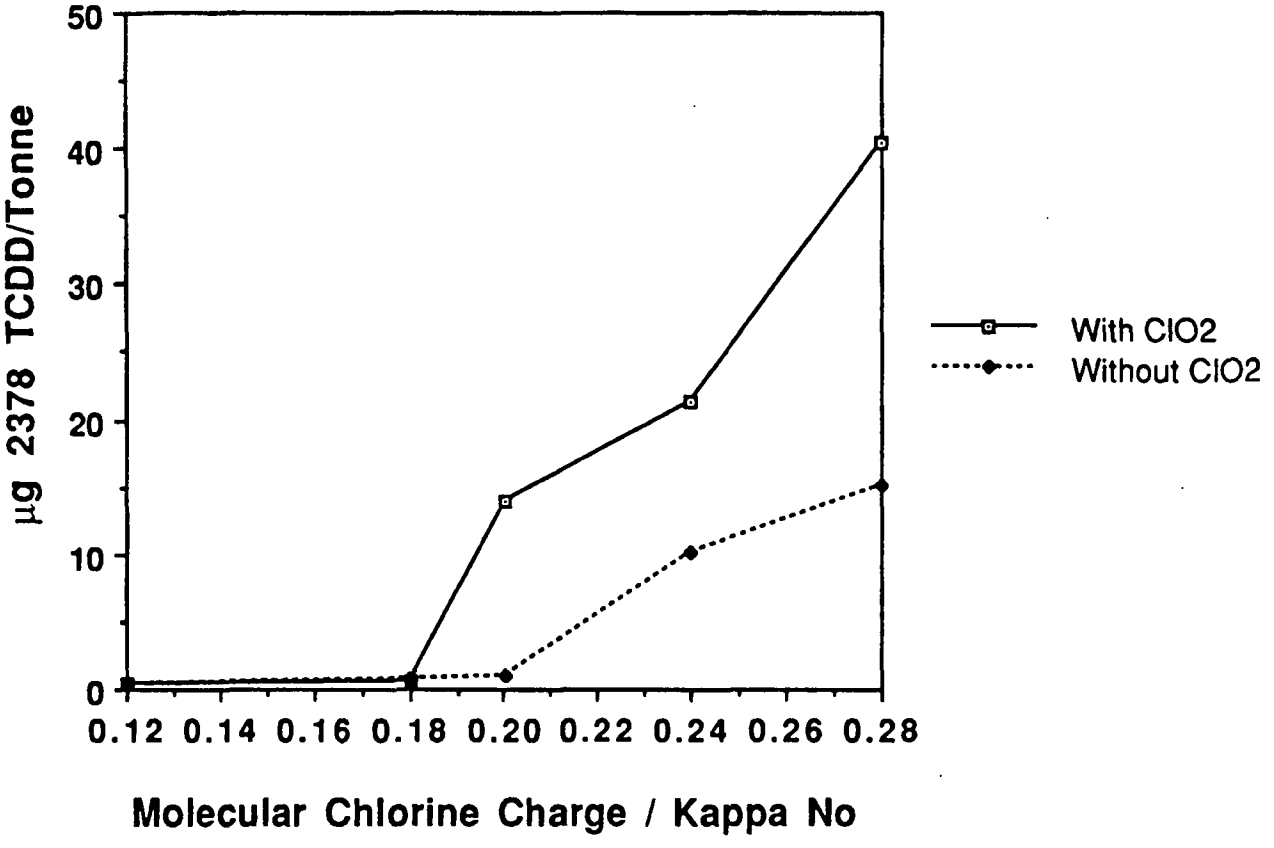

Figure 4. 2378-TCDD formed as a function of molecular chlorine applied, with and without ClO_2 pretreatment.

The mechanism by which chlorine dioxide pretreatment increases the formation of dioxins during subsequent chlorination is not yet known. Three possibilities suggest themselves. The first is that, because chlorine dioxide satisfies part or all of the lignin's chlorine demand, less chlorine reacts with lignin and more is available for conversion of precursors to dioxins. The second is that chlorine dioxide generates precursors, for example by liberating DBD or forming some other precursor from lignin. The third, and least likely, in view of the known beneficial effect of chlorine dioxide substitution in reducing dioxin levels, is that it converts precursors to dioxins. We hope to be able to do additional experiments to determine which of these phenomena accounts for the observations.

EFFECTS OF CHLORINATION STAGE VARIABLES AND THEIR INTERACTIONS

Intensive research on dioxins formation at IPST, NCASI and elsewhere has shown that limiting the amount of chlorine applied is an effective means of reducing dioxins to nondetectable levels. This approach has drawbacks, however, in that considerable expense is usually involved. It is therefore of interest to know how to operate the chlorination stage to minimize dioxins formation at any given level of chlorine application. Since information on interactions between chlorination process variables is needed to make this possible, we undertook a laboratory study of the effects of changes in these variables, alone and in combination.

Table 4 lists the variables we studied and the various combinations of their levels. Chlorine dioxide was added either 15 seconds before or 15 seconds after chlorine; the temperature of the stage was either 30° or 60° C; the fraction of chlorination stage filtrate recycled was either 0 or 30%; oxygen delignification was either not used or used to remove about 40% of the lignin in the unbleached pulp before chlorination; and the unbleached pulp was either perfectly washed or received normal mill washing (6 mL of dilute black liquor remained with each gram of pulp).

TABLE 4. Experimental Design for C-Stage Variable Study.

Var. Level Comb.	ClO_2 Sec. Aftr. Cl_2	Temp. Deg. C	C-St. Filt. Rcyc. %	Oxygen Delig. %	Wash Loss L/kg
1	-15	30	0	0	6
2	15	30	0	0	0
3	-15	60	0	0	0
4	15	60	0	0	6
5	-15	30	30	0	0
6	15	30	30	0	6
7	-15	60	30	0	6
8	15	60	30	0	0
9	-15	30	0	40	0
10	15	30	0	40	6
11	-15	60	0	40	6
12	15	60	0	40	0
13	-15	30	30	40	6
14	15	30	30	40	0
15	-15	60	30	40	0
16	15	60	30	40	6

Combinations of these levels were chosen according to a fractional factorial experimental design, and the entire series was duplicated to allow firm conclusions to be drawn. In each case, the chlorinated pulp was analyzed for dioxins by NCASI.

An important feature of this experiment was the fact that analysis was not limited to the 2,3,7,8- dioxin and furan isomers. All pulps were subjected to "full congener" analysis of numerous isomers of tetra- through octachlorinated dibenzodioxins and dibenzofurans. Analysis of the resulting extensive database is currently in progress, and may be expected to provide insight into the mode of dioxins formation in addition to the empirical information primarily sought.

For any given isomer, the structure of the experiment allows the amount formed to be related to the levels of the variables characterizing the stage. Statistical significance tests can be used to screen out unimportant effects and interactions, resulting in simplified predictive equations that summarize the important effects.

As an example, consider the analysis of the 2378-TCDD data. Although the general level of dioxins formed from the particular unbleached pulp used was quite low, several significant effects were observed. The most important were those of oxygen delignification and order of addition of chlorine and chlorine dioxide. An interaction (dependence of the effect of one variable on the level of the other) between these two was also significant.

The average levels of 2378-TCDD observed under the various conditions of these two variables are shown in Table 5. Each figure is the average of analyses of chlorinated pulps from 8 different bleaches; differences between them represent statistically significant effects. The level was reduced from 4.5 to 0.5 ppt by introducing an oxygen stage, and from 4.5 to 1.2 by reversing the order of chlorine and chlorine dioxide addition. The combined effect of introducing oxygen bleaching and reversing the order of addition of chlorine and chlorine dioxide is not much greater than the effect of making either change without the other. This observation is manifested in the significance of the interaction referred to above. The practical implication is to try reversing the order of addition before planning the large capital outlay associated with an oxygen stage.

TABLE 5. Effects of Sequence of Addition and Oxygen Delignification on 2378-TCDD Level.

	2378-TCDD, µg/Tonne	
	No Oxygen Stage	**With Oxygen Stage**
ClO_2 Added First	4.5	0.5
Cl_2 Added First	1.2	0.2

Other Conditions: Temp. 45°C; No Recycle; Normal Washing

FURTHER WORK

We expect to continue our studies of dioxin formation after completing analysis of the extensive database resulting from the process variable experiments. Further studies will be directed at elucidating effects of consistency and degree of mixing, and at following up on the observations described above. The latter category will include investigations of the effect of chlorine dioxide treatment on DBD/DBF levels, the mechanism of the chlorine dioxide pretreatment effect, and the nature of the nonextractable precursors. In addition, more fundamental studies of the chemistry of formation and destruction of dioxins and their precursors are underway.

SUMMARY AND CONCLUSIONS

The collaboration between IPST and NCASI has resulted in a significant increase in our understanding of the factors affecting dioxins formation in kraft pulp bleaching. We have shown that extractable DBD and DBF are not the only important precursors, that dioxins formed in the extraction stage stay with the pulp entering the extraction stage, that there is no appreciable formation or destruction of dioxins in the extraction stage, and that more than half of the dioxins emerging from the extraction stage are found in the filtrate from washing. Investigation of the mode of action of chlorine dioxide has shown that, in alleviating dioxins formation, chlorine dioxide very probably does not function by destroying precursors, and that it in fact promotes dioxin formation if it is added before chlorine and the chlorine charge is not reduced. The mechanism of this effect is not known, but it could be due to generation of new precursors, elevation of chlorine residual, or even to conversion of precursors to dioxins, although this last possibility seems unlikely. Studies of the effects of chlorination stage process variables have shown that oxygen delignification and sequence of chlorine and chlorine dioxide addition have the greatest effects, while other variables have smaller, but discernible effects. In general, the effects interact, each depending on levels of the other variables. Further analysis of effects on the formation of a large number of other dioxin and furan congeners is expected to provide insight into the origin of these classes of compounds in pulp mill systems.